

Enhancing Vinyl Chloride Product Yield by Optimizing Operating Conditions In Plug Flow Reactor With Al_2O_3 Catalyst

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Abstract

Vinyl chloride (VC) is a colorless stable gas produced through a complex process with many interactions in reaction and separation. This study aims to improve mass and energy efficiency in vinyl chloride production through process simulation with HYSYS V.11. The process was modified using a plugged flow reactor (PFR) with an Al_2O_3 catalyst and a simplified distillation column. The method involves recycling the liquid product from the distillation column back to the mixing unit as a feed. The results show that energy efficiency improves with the reduction of the reactor's heat flow requirement from 1.009×10^7 kJ/h, and to 4.689×10^6 kJ/h, and distillation of the 2.82×10^6 kJ/h to 1.368×10^6 kJ/h. Mass efficiency also increased, with vinyl chloride yields rising by 118%, from 2572 kg/h to 3045 kg/h. In conclusion, these process modifications have succeeded in reducing energy consumption and increasing production significantly, making the process more efficient and energy friendly. Further research is suggested to optimize the use of waste heat.

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Keywords: Vinyl chloride; chlorination; energy efficiency; mass efficiency; Al_2O_3 catalyst

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1. Introduction

The main use for vinyl chloride (CAS No. 1704-01-6) is the production of polyvinyl chloride, a colorless, flammable gas with a moderate, sweet smell [1]. Vinyl chloride (VC) is produced only for the purpose of polymerizing it into polyvinyl chloride (PVC), a plastic used in the transportation, electrical, construction, in household goods like water pipes, and in medical devices like bedpans [2]. Vinyl chloride can be produced using a variety of techniques, including methane oxidative chlorination [3], oxychlorination [4], catalytic chlorination [4], and electrolysis membrane process [5]. However, these techniques still have many drawbacks, including the inability to control the reaction [6], so extra steps such as the addition of Al_2O_3 catalysts are

required. Al_2O_3 catalysts in the vinyl chloride manufacturing process are used to accelerate and control reactions which can show high crushing efficiency so that it requires less heating, is more cost-effective compared to conventional thermal combustion, which requires higher operating temperatures [7]. Therefore, this study aims to accelerate the production process of vinyl chloride by using plug flow reactor and improve the efficiency of the separation mass by recycling HCl .

2. Methods

2.1 Basic Process Description

The direct chlorination method is the selected process for vinyl chloride. Currently, the direct chlorination process is often considered the most commonly used method because of its high conversion efficiency [9], i.e. direct chlorination of ethylene compounds to produce 1,2-

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dichloroethane (EDC) [10] (Figures 1 and 3). Hydrogen chloride should be carefully recycled and designed into a balanced process because it is the major byproduct of ethane chlorination in the absence of oxygen. Although hydrogen chloride can be used as a reagent or a co-reagent with chlorine for the chlorination of ethane in the presence of oxygen, the standing problems with selectivity control, carbon emission, etc., add to the complexity of the reaction design [11]. The raw materials used are ethylene and chlorine. The integrated route consists of adding a recycling unit covering unreacted feed gases for further reaction to achieve 99% conversion. By their stoichiometric ratios and at a temperature of 242 °C, pressure of 26 atm, and molar flow of 83.47 kgmol/h, ethylene and chlorine are fed into a plug flow reactor (PFR-100) pressurized at 26 atm. Specifically, the type of reactor used in the industry is a plug flow reactor (PFR), which allows the reactants to flow continuously through the 1,2-dichloroethane (EDC) liquid heated to a temperature of 65°C. This type of reactor can maximize the mass transfer of ethylene. The resulting product is 1,2-dichloroethane (EDC).

2.2 Simulation with Aspen HYSYS

A model-based depiction of chemical, physical, and other technical processes and unit operations is called process simulation [12]. The rough replication of a process that mimics its operation over time is called simulation. In scientific modeling of chemical systems, simulation is often utilized to gain insight into the behavior or function of the specific system. It illustrates the ultimate, tangible results of various circumstances and strategies [13]. Pharmaceutical, chemical, petrochemical, oil, refining, gas sweetening, and other industries find good use for Aspen HYSYS, a process simulator for conceptual design [14]. One of the fundamental components of a simulation is the HYSYS property package. Property packages are useful for illustrating how components behave and interact with one another. In a simulation, choosing the right property package is essential. Selecting the wrong property package might lead to inaccurate simulation results or even prevent the simulation from running. A set of unique techniques for determining parameter values and component qualities in simulations is known as the property package [15]. Peng Robinson is the

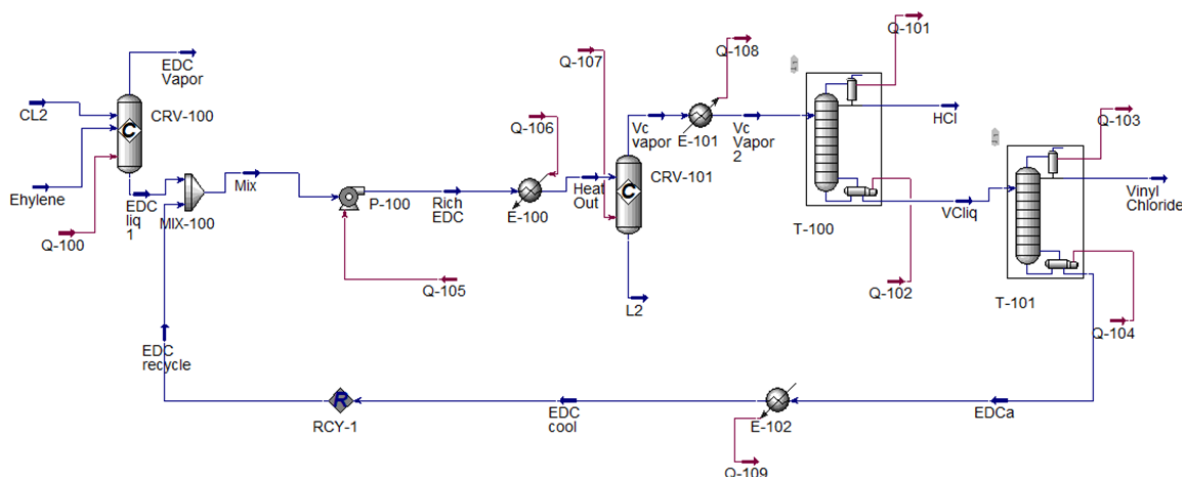


Figure 1. Simulation vinyl chloride production before modified with Aspen HYSYS V11

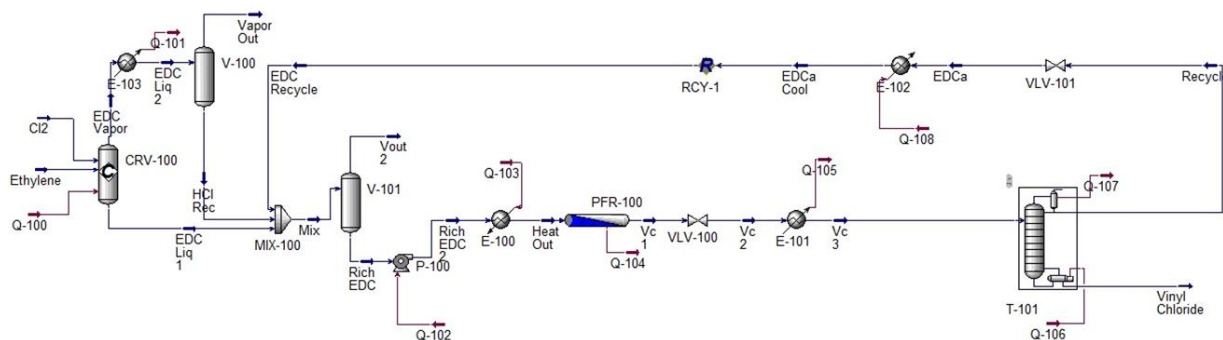


Figure 2. Simulation vinyl chloride production after modified with Aspen HYSYS V11

property package utilized in this simulation. This model is perfect for determining liquid density for hydrocarbon systems and for VLE calculations [16]. The HYSYS simulation and the modified process flow diagram of vinyl chloride production is shown in Figures 2 and 4, respectively.

3. Results and Discussion

3.1 Effects of Process Creation for Energy Efficiency

Distillation has been the separation workhorse for the Chemical Process Industries (CPI) for over a century and is by far the most important separation method used, with about 90–95% of all separations in the chemicals and petroleum refining industries [17]. To improve energy efficiency, the equipment we simulated is less complicated by using only one distillation column and a plug flow reactor when compared to the previous equipment that used two conversion reactors and two distillation columns. The heat flow required by the conversion reactor before

modification is 1.009×10^7 kJ/h. Meanwhile, the heat flow required by the plug flow reactor after modification is 4.689×10^6 kJ/h. The reactor's heat flow before and after process modification is shown in Table 1. In addition, the heat flow required by the distillation tower to produce vinyl chloride products before modification is 2.182×10^6 kJ/h. Meanwhile, the heat flow required by the distillation tower after modification is 1.368×10^6 kJ/h. The distillation column's heat flow before and after process modification is shown in Table 2. So, the heat flow on the equipment after modification tends to be smaller than the heat flow on the equipment before modification.

3.2 Effects of Process Creation for Mass Efficiency

To improve mass efficiency, we added a cooler (E-103) to partially condense the upper product of the CRV-100 reactor. A cooler is a device used to lower the temperature of a fluid or gas by transferring heat to a cooling medium,

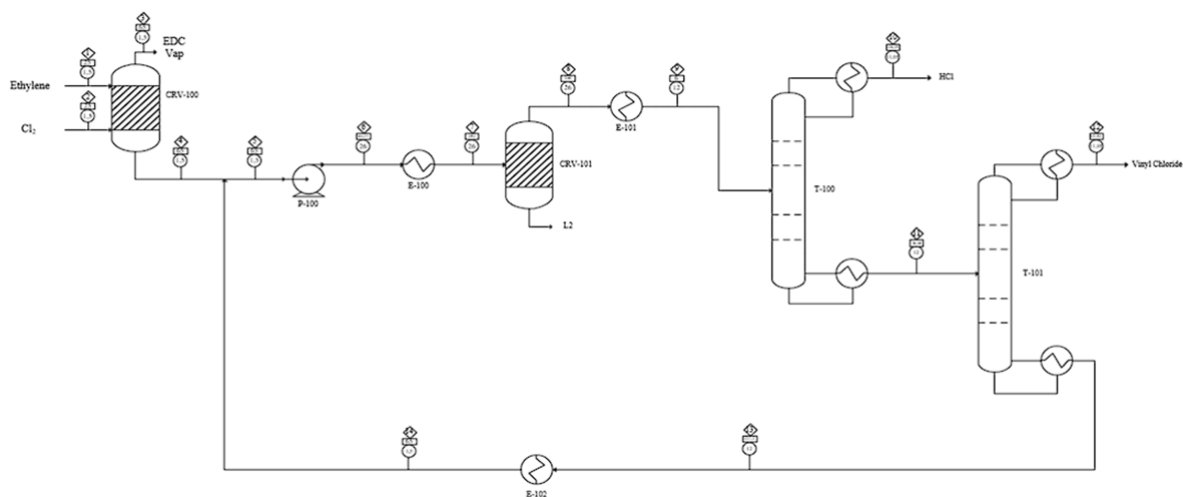


Figure 3. Process flow diagram of basic vinyl chloride production process

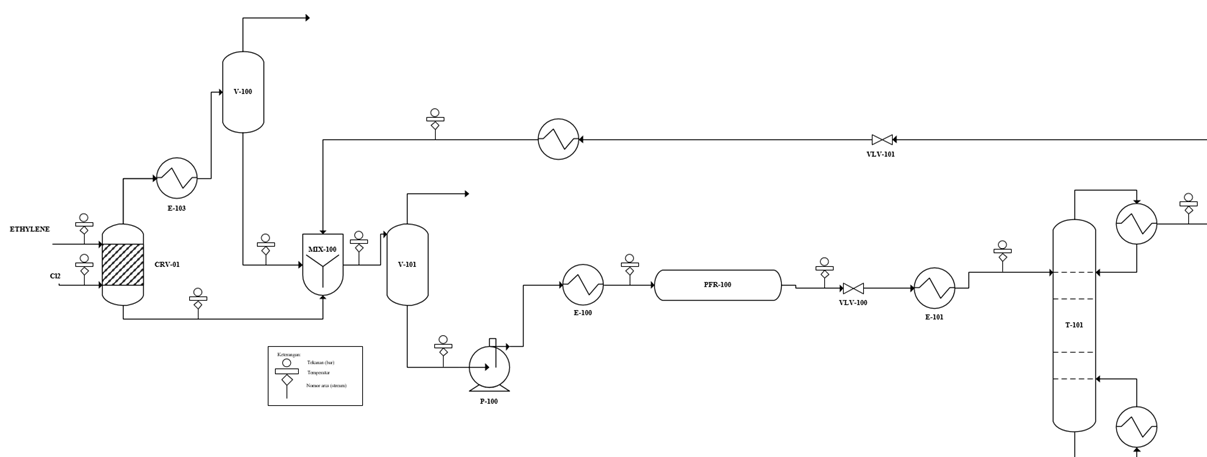
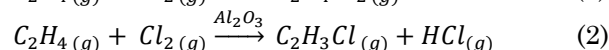
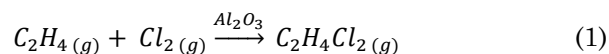


Figure 4. Process flow diagram of modified vinyl chloride production process

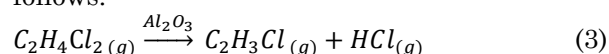
such as air or water [18]. After that, it enters the flash drum separator to separate the liquid phase and vapor phase. The liquid phase with abundant EDC content is fed into the feed stream to increase the mass rate of the feed from 4109 kg/h to 18490 kg/h. In the end, it produces a much larger product in the modified result from 2572 kg/h to 3045 kg/h vinyl chloride. Mass and energy balance of simulated modified process is reported in Table S1 (Supporting Infirmination). Menawhile, the overall mass balance of system before and after modification is shown in Figure 5 and Figure 6.

3.3. Description of the Modified Process

The raw materials used are ethylene and chlorine. The integrated route consists of adding a recycling unit covering unreacted feed gasses for further reaction to achieve 99.9% conversion. By their stoichiometric ratios and at a temperature of 242 °C, pressure of 26 atm, and molar flow of 83.7 kgmol/h. The raw materials used are ethylene (C_2H_4) and chlorine (Cl_2) are fed into a conversion reactor (CRV-100). The reactor product is then mixed with recycle (RCY-1) in a stirrer (MIX-100). This mixture is then separated in a separator (V-101), producing a liquid phase rich in ethylene dichloride (EDC) as the main product. The EDC-rich liquid is pumped through a pump (P-100) and heated using a heater (E-100) to achieve the optimal reaction temperature before entering the plug flow reactor (PFR-100). In this reactor, the main reaction occurs with the help of the catalyst alumunium oxide (Al_2O_3), which acts as a Lewis acid catalyst under specific operating conditions. The reactions that occur are as follows:

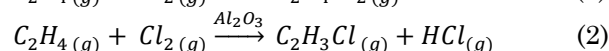
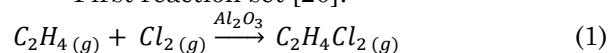


The Al_2O_3 catalyst is used to accelerate the reaction and increase selectivity towards EDC formation with high efficiency [19]. The output from the reactor (PFR-100) is cooled using a heat exchanger (E-101), then directed to the distillation process in the distillation column (T-101). This column separates the product into EDC gas in the overhead stream and vinyl chloride in the bottom stream. The EDC is reused in the process as a feed for circulation through a recovery line using a valve (VLV-100) and cooled in a heat exchanger (E-102). The bottom product from the distillation column is used as the final product because it contains 1,2-dichloroethane (EDC) with sufficiently high purity. The EDC, which has been purified, achieves a purity level of 99.9% in the distillation column (T-101). The reaction process that occurs can be explained as follows:



3.4 Thermodynamics Aspects

First reaction set [20]:



ΔG for reaction (1) = 5.73 kJ/mol

ΔG for reaction (2) = -120.49 kJ/mol

ΔH_{298} for reaction (1) = -182 kJ/mol

ΔH_{338} for reaction (1) = -180.548 kJ/mol

ΔH_{298} for reaction (2) = -116.15 kJ/mol

ΔH_{338} for reaction (2) = -114.527 kJ/mol

Table 1. Reactor's heat flow before vs after process modification

Heat flow before modification	Heat flow after modification
1.009×10^7 kJ/h	4.689×10^6 kJ/h

Table 2. Distillation column's heat flow before vs after modification

Heat flow before modification	Heat flow after modification
2.182×10^6 kJ/h	1.368×10^6 kJ/h

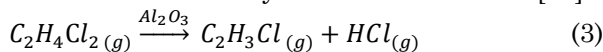
Inlet Material Streams	Counted	Mass Flow	Outlet Material Streams	Counted	Mass Flow
CL2	☒	7091 kg/h	EDC Vapor	☒	5787 kg/h
Ethylene	☒	2805 kg/h	L2	☒	0,0000 kg/h
			HCl	☒	1533 kg/h
			Vinyl Chloride	☒	2572 kg/h

Figure 5. Overall mass balance of system before modification

Inlet Material Streams	Counted	Mass Flow	Outlet Material Streams	Counted	Mass Flow
Ethylene	☒	2805 kg/h	Vout 2	☒	1,091e+004 kg/h
Cl2	☒	7091 kg/h	Vinyl Chloride	☒	3045 kg/h
			Vapor Out	☒	576,1 kg/h

Figure 6. Overall mass balance of the modified process

From Gibbs free energy from the first reaction set that reaction (1) is not spontaneous. We also know from delta enthalpy that reaction occurs exothermically. Second reaction set [20]:



ΔG for reaction (3) = -126.22 kJ/mol

ΔH_{298} for reaction (3) = 65.85 kJ/mol

ΔH_{338} for reaction (3) = 64.923 kJ/mol

From Gibbs free energy from the second reaction set that reaction (3) happens spontaneously. We also know from delta enthalpy that reaction occurs endothermically.

4. Conclusion

From simulations it can be concluded that we have modified the process of making vinyl chloride using the direct chlorination method so that it becomes more efficient in terms of mass balance (with the same amount of feed can provide more product) and less energy use. From the simulations that have been carried out to increase mass efficiency, it is found that the yield of vinyl chloride products obtained increases significantly by about 118% that the yield of vinyl chloride products obtained increases rapidly by about 118% from 2572 kg/h to 3045 kg/h. On the other hand, for the improvement of energy efficiency in reactor, it was found that the energy demand for reactor decreased from 1.009×10^7 kJ/h to 4.689×10^6 kJ/h. For the improvement of energy efficiency in distillation column, the energy decreased from 2.182×10^6 kJ/h to 1.368×10^6 kJ/h. Suggestions for future research, namely further processing is needed to optimize the process by utilizing exhaust heat. That's will make the process more effective and efficient.

CRedit Author Statement

Author Contributions: A. Fauziyah: Conceptualization, Methodology, Investigation, Software, Visualization, Project Administration, Supervision; I. Ratnawati: Conceptualization, Methodology, Data Curation, Writing, Review & Editing, Validation; M.R.L. Shafura: Conceptualization, Methodology, Formal Analysis, Resources, Validation, Review & Editing, Writing; W.A. Anggraini: Conceptualization, Methodology, Investigation, Resources, Data Curation, Review & Editing, Writing. All authors have read and agreed to the published version of the manuscript.

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